

Improved ground state rotational constants for the argon–hydrogen fluoride dimer

Paul A. Stockman

*Division of Chemistry and Chemical Engineering, California Institute of Technology 170-25,
Pasadena, California 91125*

Geoffrey A. Blake

*Division of Geological and Planetary Sciences, California Institute of Technology 170-25,
Pasadena, California 91125*

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In the past decade, the intermolecular potential of the argon–hydrogen fluoride dimer (Ar–HF) has been probed by microwave spectroscopy of the vibrational ground state^{1–3} and by intramolecular^{4–7} and intermolecular^{5–9} spectra of the HF fundamental stretch and van der Waals modes. Also, the intermolecular potential energy surface (IPS) of the Ar–HF molecule has been the focus of several theoretical^{10,11} studies. While the ground state has been probed directly by microwave spectroscopy only to the $J=3$ level, subsequent infrared studies have measured transitions arising from the ground vibrational state with rotational energies up to $J=40$, albeit with a nearly thousand-fold decrease in experimental precision. Analyses of these infrared spectra have required Hamiltonians containing high-order centrifugal distortion constants due to large amounts of anharmonicity in the high- J rotationally predissociative states.⁵

As experimental and theoretical studies probe ever higher regions of the IPS, the need for improved ground state rotational constants becomes apparent. Indeed, a number of new experimental techniques have recently been developed to probe the overtone spectra of clusters for which the availability of accurate ground state term values would greatly aid in the assignment and fitting of the data.^{9,12} We therefore present here extended microwave and millimeter-wave measurements of the ground vibrational state rotational transitions up to $J(13 \leftarrow 12)$. A combined weighted fit with previously measured rotational transitions^{1(b)} and high- J infrared spectra (10^0) \leftarrow (00^0) (excitation of the HF monomer)⁵ is used to extract an expanded set of ground state rotational constants with improved precision and accuracy. The resulting term values have proven useful in fits of the third overtone spectra of Ar–HF obtained by Chang and Klemperer.¹²

The experimental apparatus employed is the same as that previously described,¹³ consisting of microwaves broadcast and received by tapered waveguide horns across the supersonic expansion through a 1.75 in. \times 0.001 in. slit. The effective cutoff of the spectrometer after applying a series of frequency doublers and triplers to the 0.01 to 20 GHz source was ~ 80 GHz. The control of the gases was also as before, using an expansion of 5.80 slm Ar and 120 sccm HF. Automated scans of the observed rotational transitions with both increasing and decreasing frequency increments were taken and averaged to eliminate errors

due to the time constant of the lock-in amplifier. Rotational transitions from $J(4 \leftarrow 3)$ to $J(13 \leftarrow 12)$ were recorded. These are presented in Table I, along with the lowest three rotational transitions previously observed.

The data were fit as in previous efforts^{5,7} to a power series in $J(J+1)$:

$$E(v, J) = v + B_v J(J+1) - D_v J^2(J+1)^2 + H_v J^3(J+1)^3 + L_v J^4(J+1)^4 + P_v J^5(J+1)^5, \quad (1)$$

with a nonlinear least-squares analysis. The rotational constants from Dixon *et al.*^{1(b)} were used to generate the three lowest transition frequencies free from the effects of spin-spin interactions. As the emphasis throughout was on obtaining the most accurate rotational constant values possible for the ground state, care was taken not to affect the lower order constants with the large anharmonicity exhibited by the high- J infrared spectra. Consequently, the microwave transitions were fit with constants up to L_0 , with the data from Dixon *et al.* being weighted with $\sigma \approx 5$ kHz and the present frequencies having an estimated error of $\sigma \approx 100$ kHz, in accordance with the measured precision of the two data sets. B_0 and D_0 were fixed at values from this fit in the combined analysis of the microwave and infrared data and the value of H_0 was made 1000 times more resistant than the other determined parameters. The infrared data set was also weighted with respect to its measured precision, with most lines having a weight of $\sigma \approx 20$ MHz. A few lines corresponding to blends in the P -branch head and transitions near interfering HF dimer lines¹⁴ were assigned larger estimated errors. The results of this fit are presented in Table II with rotational constants for both the ground, $v(\text{HF})=0$, and (10^0), $v(\text{HF})=1$, vibrational states.

Considering first the results from the fit of the microwave data sets in Table I, a comparison of the present rotational constants with those from previous high resolution studies of the lowest few transition frequencies reveals no discrepancy in the B_0 values within $\pm \sigma$. The first distortion term D_0 is approximately 1% smaller than earlier reported values, having been partially freed from the effects of higher-order distortion by a well-determined H_0 value, while at the same time benefiting from the contributions of higher- J transitions. Constants through L_0 were necessary

TABLE I. Measured microwave transition frequencies (MHz) and fitted rotational constants (MHz) for Ar-HF.

J''	J'	Measured	Residual ^a
0	1	6 131.132 ^b	0.002
1	2	12 260.565 ^b	0.000
2	3	18 386.601 ^b	-0.001
3	4	24 507.58	0.05
4	5	30 621.66	0.05
5	6	36 727.10	0.02
6	7	42 822.16	-0.01
7	8	48 905.04	-0.02
8	9	54 973.88	-0.01
9	10	61 026.82	0.06
10	11	67 061.70	-0.04
11	12	73 076.87	-0.01
12	13	79 070.17	0.01

Constants	Fitted Values
B_0	3065.7063(43)
D_0	$0.70578(89) \times 10^{-1}$
H_0	$-0.894(69) \times 10^{-5}$
L_0	$0.40(18) \times 10^{-8}$

^aResidual=observed-calculated.^bGenerated from constants of Ref. 1(b); see text.

in order to bring the fit to the level of experimental uncertainty.

The global fit combining both microwave data sets and the $(10^0_0) \leftarrow (00^0_0)$ infrared data of Fraser and Pine⁵ is essentially the splicing of two polynomial functions. The preferential weighting of the microwave data ensures that the pure rotational frequencies contribute more to the determination of the lower-order ground state terms and the high- J infrared data weigh more heavily in the determination of the two highest-order ground vibrational state terms L_0 and P_0 . While significantly different from those determined by Fraser and Pine, the set of constants given in Table II are qualitatively similar in magnitude and sign as expected. However, the same comparison cannot be made with the constants obtained by Lovejoy and Nesbitt.⁷

TABLE II. Globally fitted rotational constants (MHz) for Ar-HF.

	$v=0$	$v=1$
B	3065.7063 ^a	3076.84(23)
D	0.70578×10^{-1} ^a	$0.6518(90) \times 10^{-1}$
H	$-0.852(51) \times 10^{-5}$	$-0.30(14) \times 10^{-5}$
L	$0.228(66) \times 10^{-8}$	$-0.171(95) \times 10^{-8}$
P	$-0.254(22) \times 10^{-11}$	$-0.62(24) \times 10^{-12}$
E_v	3951.768 42(55) cm ⁻¹	

^aFixed at value from Table I.

Their observation of the rovibrational $(10^0_0) \leftarrow (00^0_0)$ band in a ~ 13 K beam limited them to measure transitions from $J \leq 27$. Both their data set and ours are insensitive to the higher-order distortion seen in the 211 K static White cell experiment of Fraser and Pine. Consequently, the ground state constants of Lovejoy and Nesbitt place the pure rotational band head for Ar-HF at $J(90 \leftarrow 91)$ as opposed to $J(60 \leftarrow 61)$ for Fraser and Pine or $J(58 \leftarrow 59)$ for the present work.

It is also interesting to note an increase in the value of the B rotational constant from the ground state to the (10^0_0) state along with a uniform decrease in the magnitudes of the associated distortion constants. This is consistent with the findings of Huang *et al.* that the first excited state of the HF monomer within Ar-HF exhibits a remarkably long vibrational predissociative lifetime ($\tau \geq 300 \mu\text{s}$) due to a shortening and stiffening of the van der Waals bond.

In conclusion, we have extended considerably the ground state microwave spectra of Ar-HF. These new transition frequencies in turn have allowed us to improve upon the existing rotational constants for the ground state by a combined fit with high- J infrared data. The errors in the term values are under 1 MHz up to $J=20$, and ≤ 30 MHz for J values up to 40.

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